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INVESTIGATION OF THE IN-SITU OXIDATION OF METHANOL IN FUEL CELL--ETC(U)

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# INVESTIGATION OF THE IN-SITU OXIDATION OF METHANOL IN FUEL CELLS

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Contract No. DAAK70-80-C-0049

June 1980 to May 1981

Final Technical Report

D.A. Landsman  
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Prepared for

U.S. Army Mobility Equipment Research and Development Command  
Fort Belvoir, VA 22060

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Direct anodic oxidation and internal reforming were examined as ways of using methanol as fuel in a phosphoric acid fuel cell.  The literature was reviewed to identify the most effective catalysts for the direct electrochemical oxidation of methanol. It was shown experimentally that, even with the best of these catalysts, anode polarization at practical current densities is 300 mV higher on methanol than on hydrogen. It was also found that unreacted methanol which diffuses across the cell can cause severe polarization of the cathode.		

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Theoretical and experimental studies of internal reforming showed that a fuel cell will generate sufficient waste heat to sustain the methanol-steam reforming reaction. Thus, thermally-integrated, internal reforming is a feasible alternative to external reforming. The reforming catalyst is preferably located in separate chambers built into the stack, since this prevents phosphoric acid from attacking the reforming catalyst and methanol from migrating to the cathode.

A 2-in. by 2-in. fuel cell, running on the gaseous product from a subscale reformer operating at 400°F, gave 0.624 volts at 200 ASF (85% methanol/50% air utilization).

From the standpoint of efficiency, internal reforming is superior to direct oxidation.

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## SUMMARY

The aim of the program was to determine the relative merits of two different ways of using methanol as a fuel in a phosphoric acid fuel cell. One approach is to oxidize methanol vapor directly at the anode of the cell, i.e., direct oxidation. The other is to pre-convert the methanol to hydrogen and carbon dioxide by passing a mixture of methanol vapor and steam over a reforming catalyst located within the anode chamber, i.e., internal reforming.

A literature search revealed that platinum, platinum-tin, platinum-titanium, and platinum-ruthenium are active as electrocatalysts for the direct anodic oxidation of methanol. Each of these catalysts was prepared in a high surface area form, supported on Vulcan<sup>®</sup> XC-72R carbon black. Teflon<sup>®</sup>-bonded, gas diffusion electrodes were made from each catalyst and evaluated at 325-400°F in a half-cell apparatus. The platinum-ruthenium bimetallic catalyst was found to be the most active, per gram of platinum, for the direct anodic oxidation of methanol vapor in phosphoric acid. Even with this catalyst, the potential of the anode on methanol is at least 300 mV higher than on hydrogen at current densities of practical interest.

A concern that methanol might react chemically with the electrolyte to form products which poison the electrode reactions, was dispelled by showing that no harmful electro-active species are formed when methanol vapor is passed over hot concentrated phosphoric acid for a period of 500 hours.

A practical problem associated with direct oxidation is the need to prevent methanol from diffusing across the cell to the cathode. This was discovered when an attempt was made to run a subscale (2-in. by 2-in.) phosphoric acid fuel cell on methanol and air. The cell, in which the electrolyte was contained in a porous matrix, ran well at high air flows; but at low flows, i.e., high oxygen utilizations, the cathode became severely polarized. One solution to this problem is to employ an ion exchange membrane as electrolyte, but this brings attendant problems of high "iR" losses and the need to operate at relatively low temperatures with very humid reactants.

The internal-reforming approach was studied both theoretically and experimentally. Calculations showed that, above a certain minimum power level, a fuel cell will generate sufficient waste heat to sustain the endothermic methanol-steam reforming reaction; cells employing this concept are designated as "thermally integrated."

The reforming catalyst may be located directly within the anode cavity or contained in separate chambers built into the cell stack in much the same way as cooling plates are incorporated into existing designs. The latter approach, employing separate reforming chambers, has certain practical advantages since the reforming catalyst is protected from corrosive attack by the phosphoric acid, and unreacted methanol is less likely to find its way to the cathode.

The feasibility of the thermally-integrated internal-reforming cell was explored by building a small tubular reformer and operating it at 400°F, i.e., the temperature at which a phosphoric acid fuel cell stack might reasonably be expected to operate. The reformer was sized to provide sufficient hydrogen to supply three to five subscale fuel cells. At 400°F, with a steam to methanol ratio of 1.3 and a space velocity of 500/h, 93% of the methanol was reformed.

After mapping the conversion efficiency of the reformer as a function of temperature and space velocity, tests were run in which a subscale phosphoric acid fuel cell was operated for several hours on the gaseous product from the reformer. Running on the reformed methanol and air at 85%/50% utilizations, respectively, the cell gave 0.624 V at 200 ASF and 400°F. The performance of the same cell, on a simulated reformed natural gas, at comparable utilizations, was 0.642 V.

This study shows that, from the standpoint of cell efficiency, it is much better to pre-reform methanol rather than to use it directly as a fuel.

It is recommended that a small stack with internal, thermally-integrated, reforming chambers be designed and tested.

## PREFACE

This report is the final technical report on Contract No. DAAK70-80-C-0049 between the U. S. Army Mobility Equipment Research and Development Command (MERADCOM), Fort Belvoir, Virginia and Power Systems Division of United Technologies Corporation (United), South Windsor, Connecticut. The work reported here was conducted from May 1980 to May 1981. The contributions of Mr. Amos Coleman, the MERADCOM technical representative, are gratefully acknowledged. Technical contributors to this program at United included D. A. Landsman, A. P. Mientek, R. D. Sawyer, F. J. Luczak, C. D. Jordan, and J. S. Larmett, Jr.



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## INTRODUCTION

Methanol-fueled power plants, based on a low-temperature steam reformer and a phosphoric acid fuel cell stack, are of interest as lightweight, silent sources of electrical power for military purposes. In this regard, United Technologies Corporation is providing the U.S. Army with sixteen 1.5-kW units under Contract No. DAAK70-80-C-0049.

From a development standpoint there are improvements which could be made to increase the efficiency of methanol power plants, to reduce their complexity and to lower their cost and weight. One approach is to eliminate the separate reformer. This might be accomplished in one of two ways:

by electrochemically oxidizing the methanol directly at the anode of the fuel cell; or,

by integrating the reforming operation into the cell stack.

The studies described in this report were undertaken to provide information needed to assess the feasibility of the above two approaches.

The program was divided into three tasks, with associated subtasks, as shown in Figure 1.

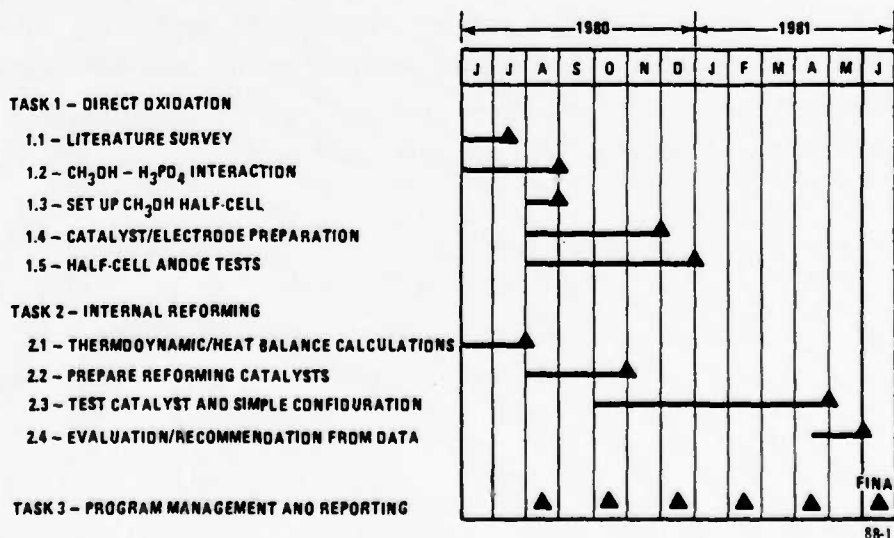


Figure 1.  
Program Schedule

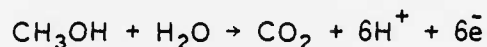
## INVESTIGATION AND DISCUSSION

## TASK 1 DIRECT OXIDATION

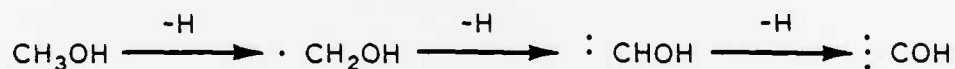
Subtask 1.1 Literature Survey

The published literature on the anodic oxidation of methanol was reviewed with particular reference to heterogeneous electrocatalysts which have been used in acidic electrolytes. The most comprehensive general articles on the subject are a review by Hampson, Willars and McNicol (1) in 1979 and a recent paper by McNicol (2).

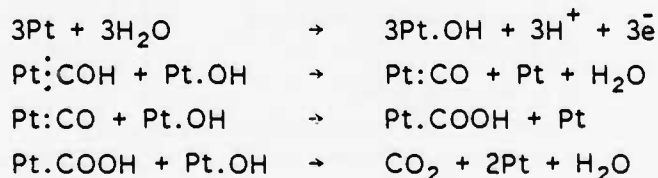
The overall electrochemical oxidation of methanol is expressed by the equation:



The reaction probably occurs by a stepwise process in which the individual hydrogen atoms attached to the carbon are successively oxidized to  $\text{H}^+$ :



The species  $\cdot \text{COH}$  is probably adsorbed very strongly on the surface of the catalyst and tends to inhibit further reaction by occupying catalytic sites. It is likely that this species is ultimately destroyed by reaction with an adjacent adsorbed water molecule (or hydroxyl group) thereby completing the oxidation.(3) On a platinum surface this final reaction may occur by the following sequence:



Based on the foregoing premise materials can only be effective catalysts for the oxidation of methanol if they are able to absorb methanol and water simultaneously at low potentials. Since platinum does not readily adsorb water in acid at low potentials, much of the work on methanol electrocatalysts has centered on platinum in association with various ad-atoms (4, 5, 6, 7), which may provide adsorption sites for water molecules. Elements which, in conjunction with platinum, have been found to be the most active for the anodic oxidation of methanol are ruthenium, tin, and titanium. It is not clear whether a true alloy or simply a bimetallic arrangement is the more active, but it is true that a platinum-based catalyst need not be an alloy to exhibit a significantly higher activity than platinum alone.

Most of the work reported in the literature was done with sulfuric acid below 100°C. Little was known about the direct oxidation of methanol in concentrated phosphoric acid at high temperatures, (i.e., >90% at 200°C). In one paper, McNicol, et.al. (8) describes a poisoning effect of phosphoric acid on a platinum-tin alloy which they attribute to a buildup of polymeric phosphate anions at the tin oxide sites. Total coverage occurred in 6-12 hours at 80°C.

On the basis of the literature search, the following four catalysts were selected for experimental evaluation:

- platinum
- platinum-tin
- platinum-titanium
- platinum-ruthenium

#### Subtask 1.2 Methanol-Phosphoric Acid Interaction

As a preliminary to testing the catalysts, experiments were done to determine if there are any chemical reactions between hot phosphoric acid and methanol vapor. Such reactions could invalidate the direct oxidation approach, e.g., the formation of esters could result in a serious loss of electrolyte through volatilization or an impairment of the electrode reactions through poisoning of the catalyst.

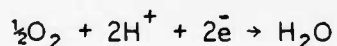
To answer this question, a stream of methanol and water vapor was passed over 99% phosphoric acid at 375°F, in the presence of platinum, for 500 hours.(9) Two methods were used to look for reaction products. In the first, both the bulk acid and the condensate from the reaction vessel were analyzed by infrared spectroscopy. No evidence was found for ester linkages between  $\text{H}_3\text{PO}_4$  and  $\text{CH}_3\text{OH}$ . In the second, a comparison was made of the performances of an electrode when run in fresh acid and in acid from the interaction test. There was no discernible difference in the ability of the electrode to promote the anodic oxidation of methanol.

It was concluded that any chemical reaction between methanol and hot phosphoric acid is so slight that it will have no practical influence on the performance or operation of a methanol-air, phosphoric acid fuel cell.

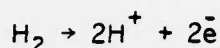
#### Subtask 1.3 Set Up Methanol Half-Cell

The method customarily used at United to evaluate an electrocatalyst is to make it into a Teflon-bonded, gas-diffusion electrode and test it in a glass half-cell apparatus as described by Kunz and Gruver.(10) This type of half-cell, with its ancillary electronic equipment, was set up to evaluate the catalysts chosen for study in this program.

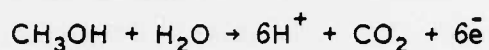
A systematic test procedure was employed to ensure that each catalyst was preconditioned in exactly the same way. This procedure consisted of first measuring the performance curve (E versus  $i/A$ ) of the electrode for the cathodic reduction of oxygen:



This step also helped to fill the catalyst with electrolyte. Next, the performance curve was determined for the anodic oxidation of the hydrogen in a gas mixture whose composition is close to that of reformed natural gas, Table 1:



This provided information on the ability of the catalyst to tolerate carbon monoxide. Finally, a performance curve was obtained for the anodic oxidation of methanol:



Several pieces from each catalyst/electrode combination were tested in this manner to ensure that the results were reproducible.

TABLE 1. SIMULATED REFORMED NATURAL GAS

GAS	PERCENT BY VOLUME
H <sub>2</sub>	70
CO	1
CO <sub>2</sub>	29

#### Subtask 1.4 Catalyst/Electrode Preparation

The catalysts tested in this program were all prepared in a high surface area, supported form. The basic catalyst was 10 wt.% Pt dispersed on a conductive carbon black--Vulcan XC-72 (ex., Cabot Corporation). The Pt/C was evaluated as a catalyst in its own right and was also the starting material from which the three bimetallic catalysts (Pt-Sn/C, Pt-Ti/C, and Pt-Ru/C) were prepared using procedures developed previously by United.

No attempt was made to measure the metal surface areas of the catalysts, instead they were compared at equivalent platinum contents, i.e., per mg of platinum.

The activity of a bimetallic or alloy catalyst is likely to vary with its composition--the relative amounts of the two constituents, their mutual solubilities, and the specific phases present. Under the terms of the present contract, it was not possible to study these variables. Instead, in preparing the bimetallic catalysts, procedures were used which were known from past experience to yield products in which the ratio of platinum to the non-noble constituent was approximately 10:1. In addition, one Pt-Sn/C catalyst and one Pt-Ru/C catalyst were prepared with a much higher content of the second metal by electrodepositing tin and ruthenium, respectively, on a Pt/C electrode.

For the half-cell tests, the catalysts were made into gas-diffusion electrodes consisting essentially of a thin layer of catalyst, mixed with Teflon, on a porous, conductive, wet-proofed, carbon substrate. A platinum loading of 0.5 mg/cm<sup>2</sup> of electrode was used throughout; the Teflon content and sintering conditions were chosen to give a catalyst layer which filled readily with electrolyte, but did not flood in the time taken to run the half-cell test.

#### Subtask 1.5 Half-Cell Anode Tests

Rates for the electrochemical oxidation of methanol were measured in the half-cell as functions of the potentials of the electrodes. Tests were run at 325°F, 375°F, and 400°F. Methanol vapor was fed to the cell in a stream of nitrogen--the methanol vapor pressure was 0.65 atmosphere (9.5 psi). The concentration of the H<sub>3</sub>PO<sub>4</sub> electrolyte was maintained at 99.5% by adjusting the dewpoint of the fuel stream. The potentials of the electrodes were measured relative to an unpolarized hydrogen electrode in the same medium.

Performance curves for the four catalysts, at 400°F, are shown in Figure 2. All of the electrodes show high polarizations at current densities of practical interest, although the alloys are more active than platinum alone. The difference in intrinsic activity between the alloys and Pt/C is even greater than appears in Figure 2, since the metal areas in the alloys were probably about half of that in the platinum catalyst.



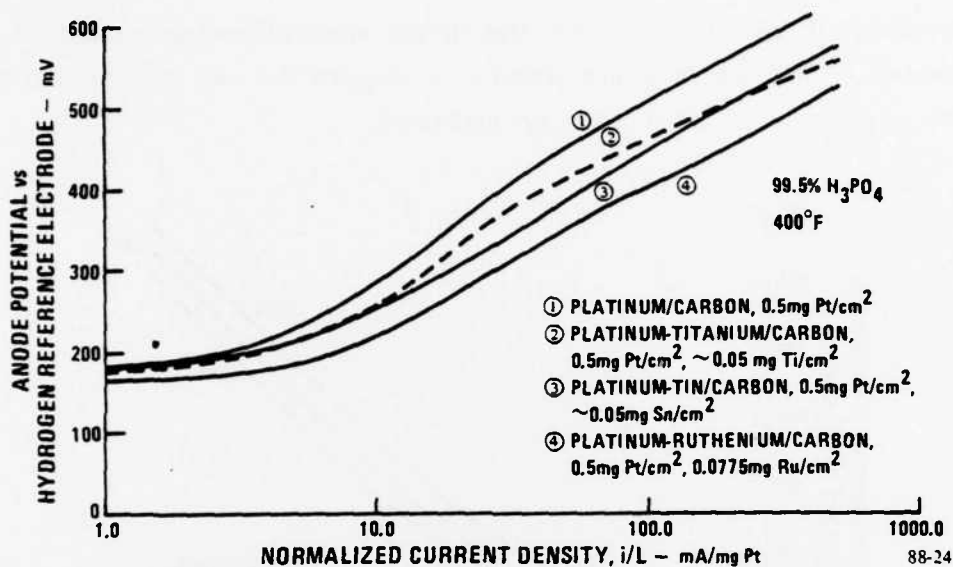


Figure 2. Comparison of Catalyst Performance for the Direct Oxidation of Methanol

The catalysts displayed increasing polarization as the temperature was decreased-- the effect of temperature on the activity of the Pt-Sn/C catalyst is shown in Figure 3.

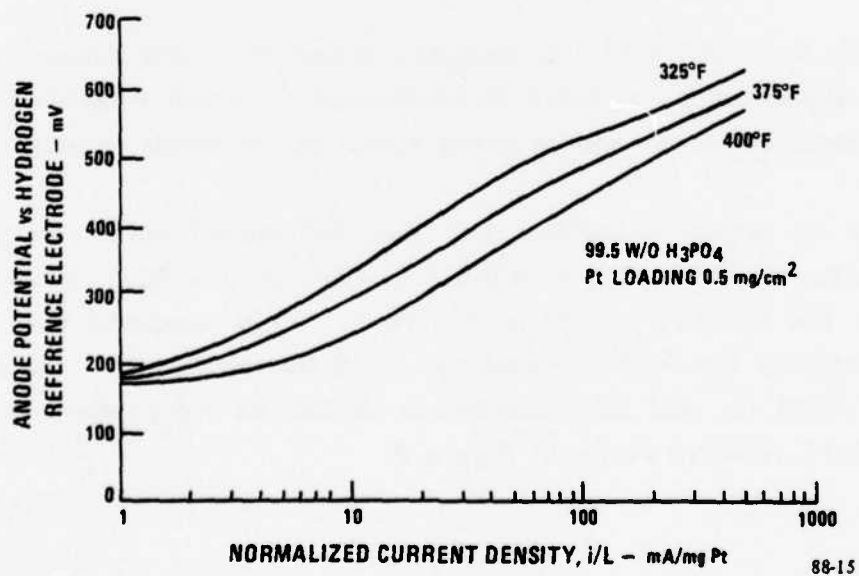


Figure 3. Direct Electrochemical Oxidation of Methanol on a Pt-Sn Catalyst

The performance of the tin alloy for the direct electrochemical oxidation of ethanol was determined. The results are shown in Figure 4. At similar conditions the polarization on ethanol is lower than on methanol.

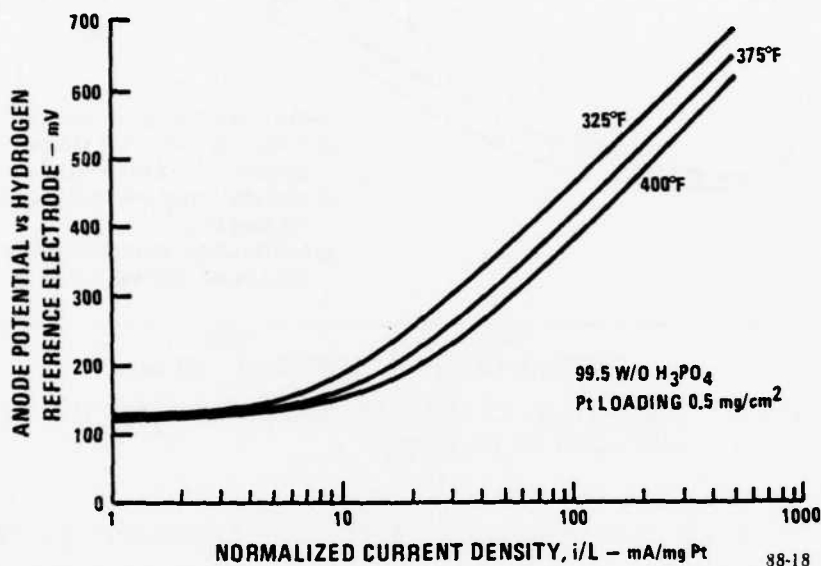


Figure 4. Direct Electrochemical Oxidation of Ethanol on a Pt-Sn Catalyst

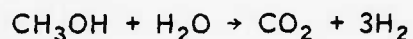
Pt-Ru/C is the most active of the catalysts examined in the present study. This conclusion is supported by a recent announcement (11) that Hitachi is proposing to market a methanol-air power source using Pt-Ru as the anode catalyst.

The electrode on which ruthenium was electrodeposited--and which contained a very high ruthenium content (44 wt%Ru:5.5 wt%Pt:50.5 wt%C) - gave lower polarizations than the Pt-Ru/C anode in Figure 2. This suggests that future work aimed at optimizing the Pt-Ru/C catalyst could be worthwhile. By contrast, the electrode on which tin was electrodeposited showed no improvement in performance over the Pt-Sn/C catalyst shown in Figure 2.

## TASK 2 INTERNAL REFORMING

Subtask 2.1 Thermodynamic/Heat Balance Calculations

As shown in Task 1, the direct electrochemical oxidation of methanol at the anode of a fuel cell is a slow and inefficient process. The approach which is commonly taken to avoid this situation is to convert the methanol first to a hydrogen-rich gas by steam reforming



In present methanol-air fuel cell power plants, the steam reforming process is usually carried out in a unit which is physically separate from the cell stacks. However, since the steam reforming reaction is endothermic, provision is made, in the interests of efficiency, to transfer as much as possible of the waste heat from the cells to the reformer module. Thus, by operating the cell stacks at 350-400°F it is possible to supply the steam requirements of the reformer.

The aim of the present task was to explore the feasibility of reducing the complexity of the system and to possibly improve the overall efficiency by integrating the steam reforming process more closely with the stack. In this phase of the program calculations were done to determine the most effective location for the reforming catalyst.

Four positions were considered:

- within the anode gas cavity
- between cells in separate reforming chambers
- within the fuel inlet manifold
- within the reactant exit manifold.

A preliminary assessment of how each of these locations would affect the operating characteristics of the power plant led to the selection of the first two for detailed

thermodynamic calculations. The first scheme--with the reforming catalyst in the anode cavity--is what is generally accepted as "internal reforming": the second--with the reforming catalyst in separate, intercell chambers--will be referred to as "thermally integrated reforming."

Estimated performances of cells incorporating both configurations are shown in Figure 5. These estimates are based on peak performances obtained from full-size phosphoric acid fuel cells running at 375°F on reformed natural gas and air, adjusted for a cell temperature of 400°F and an oxygen utilization of 50%. It was assumed that the performance of the anodes was unaffected by the presence of methanol or its reaction products.

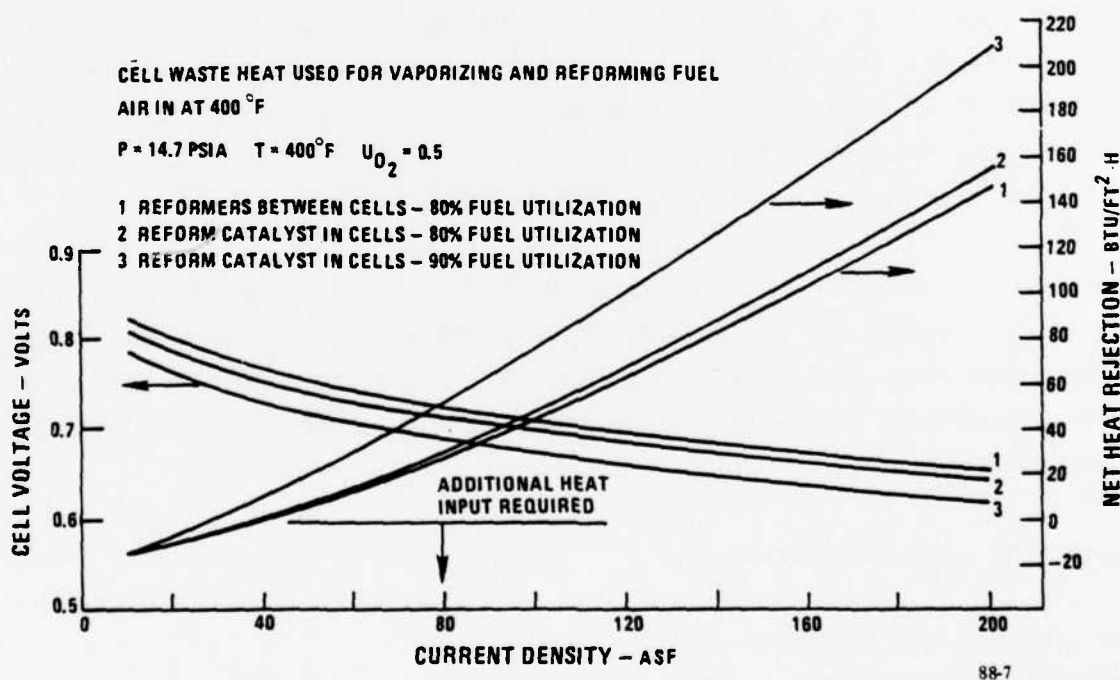


Figure 5. Estimated Performance and Net Heat Rejection for Internal-Reforming Cells on Methanol Fuel

The waste heat generated by the cells was calculated on the assumption that the reactants are supplied at 400°F and that the cells operate isothermally at this temperature. In calculating the energy required to process the fuel it was assum-

ed that the water/methanol feed, which is initially at 70°F, is reformed to a gaseous fuel at 400°F. A nominal heat loss of 20 Btu/ft<sup>2</sup>-h was assumed. On the basis of the foregoing, net heat rejection was calculated as a function of current density. These results are also shown in Figure 5.

The curves in Figure 5 show two noteworthy features: (1) At the same utilization a cell with thermally integrated reforming gives about 10 mV higher performance than a cell with internal reforming--due to a higher average hydrogen partial pressure (0.5 atm versus 0.3 atm). (2) The net heat rejection drops to zero at about 40 ASF so that heat must be supplied to the system to maintain current densities below this value.

The advantage of locating the reformer catalyst within the cell stack is shown in Figure 6 in which specific fuel consumption is plotted as a function of current density. The single point in the upper right corner of the graph indicates the specific fuel consumption at 200 ASF with no thermal integration. It should be noted, however, that the specific fuel consumptions shown in Figure 6 may not be realized in practice because they include no allowance for parasite power required to operate ancillary equipment such as pumps or fans.

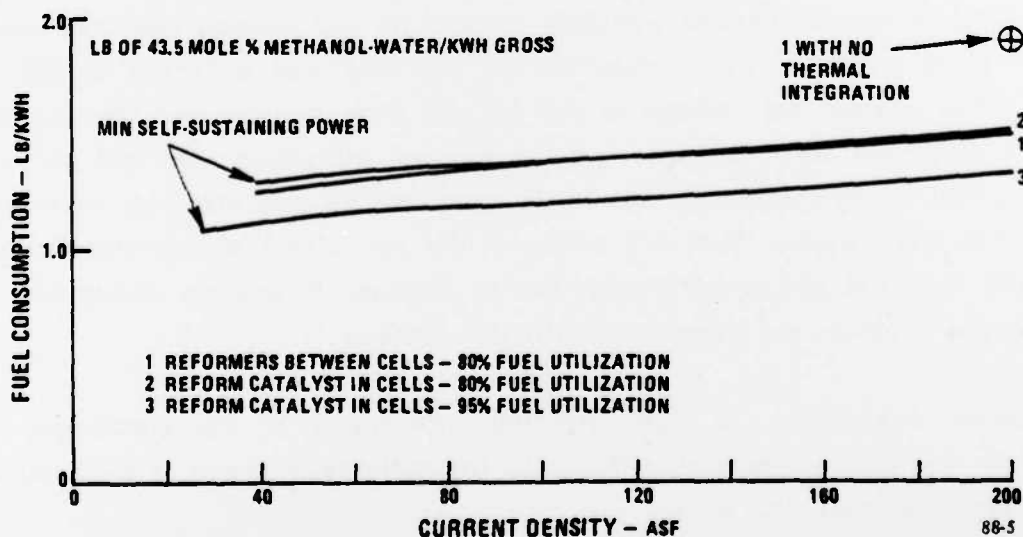


Figure 6. Specific Fuel Consumption for Internal-Reforming Cells on Methanol Fuel

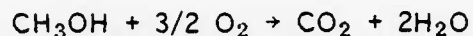
It was concluded that neither of the two schemes studied has a clear-cut advantage over the other in regard to efficiency or simplicity. However, there were unanswered questions of a practical nature concerning the internal reforming approach, e.g., (i) does the presence of unreacted methanol in the anode cavity interfere with the electrochemical oxidation of hydrogen?, (ii) how much of the methanol entering in the fuel stream is lost, by dissolution in the electrolyte and migration to the cathode, before it has a chance to participate in the steam-reforming reaction?

The first of these questions was answered by an experiment in which the half-cell apparatus was used to obtain polarization curves, first for the oxidation of hydrogen alone, and then for the oxidation of hydrogen diluted with methanol vapor.

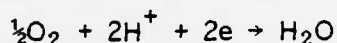
This test showed that there was no increase in anode polarization--greater than would be expected from the Nernstian loss due to the reduction in hydrogen pressure--when up to 21% of the hydrogen was replaced by methanol.

Concern over the possible loss of methanol was addressed by running a subscale fuel cell first on hydrogen and then on hydrogen diluted with methanol vapor. In both cases the cell was run at 50 ASF with air supplied to the cathode at a rate such that the oxygen utilization was 80%. When the cell voltage had stabilized with hydrogen alone as fuel, the composition of the fuel was switched to 79%  $H_2$ :21%  $CH_3OH$ . This caused the voltage of the cell to drop rapidly and then to oscillate between 0 and +300 mV. By lowering the oxygen utilization, the cell performance improved until, at 7% utilization, the initial performance and stability were restored. Since it had been shown that 21% methanol did not affect the polarization of the anode, and that the cell decay responded to changes in oxygen utilization, it was clear that the problem was associated with the cathode.

The probable explanation is that methanol introduced in the anode gas stream dissolves in the electrolyte and diffuses to the cathode where it is oxidized chemically to carbon dioxide and water.



The initial loss in cell voltage is due to a rapid drop in the oxygen partial pressure as the oxygen in the air supply is consumed in the above process. The oscillatory behavior results from the cathode slipping in and out of limiting current as a result of oxygen starvation. On increasing the air supply, i.e., running at lower utilization, sufficient oxygen is provided not only to oxidize all of the methanol reaching the cathode, but also to support the electrochemical reduction.



Support for this hypothesis was obtained by analyzing the cathode exit gas, by means of a chromatograph, while the cell was operating (at 50 ASF) on the hydrogen-methanol fuel mixture at a nominal 80% oxygen utilization. Based on the current density plus the  $\text{CO}_2$  content of the cathode effluent, the actual oxygen utilization was around 90%.

The exit gas was also passed through an ice-cooled trap to collect condensible material. Neither methanol nor formaldehyde was detected in the condensate indicating that methanol passing through the cell was totally destroyed by oxidation at the cathode.

The above results show that the anode compartment reforming approach is probably not viable unless provision is made to prevent methanol from migrating across the cell, e.g., by employing an ion exchange membrane as the electrolyte. For this reason the thermally integrated reforming approach, which reforms the methanol before it comes in contact with the anode, was selected for experimental evaluation.

#### Subtask 2.2 Prepare Reforming Catalyst

A commercially-available, copper catalyst (United Catalyst Corporation T2130) which had been evaluated previously by United under Contract No. DAAK70-77-C-0195 appeared to be a good choice for use in trials of the thermally integrated

reforming module. This catalyst is available in the form of 1/4-in. pellets and no further preparation was necessary.

### Subtask 2.3 Test Catalyst and Simple Configuration

One possible configuration for a methanol/air, phosphoric acid, fuel cell power plant with thermally integrated reforming resembles the present UTC liquid-cooled, fuel cell stack. The main difference would be that the coolers, which are built into the stack, would be replaced by reforming chambers, at a frequency of one chamber per five cells, for example. Provision would have to be made to transfer some of the product steam from the cathode effluent gas to the reformers and to add methanol vapor at an appropriate rate. However, the design and construction of such a system is beyond the scope of the present contract. Instead, a much simpler set-up was devised to demonstrate that methanol can be steam reformed at 400°F to yield a fuel of acceptable quality to run a fuel cell. The test rig is shown schematically in Figure 7. To obtain the maximum conversion of the methanol it is customary to supply steam in excess of the stoichiometric amount required by the equation:

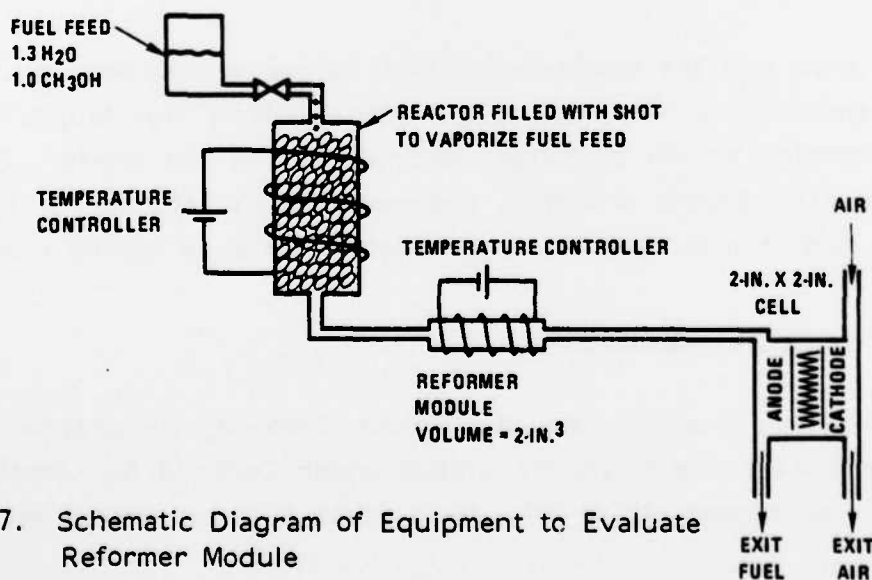


Figure 7. Schematic Diagram of Equipment to Evaluate Reformer Module

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In the tests described here a mole ratio of  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  of 1.3 was used. A liquid mixture of this composition was prepared and fed, by means of a syringe pump, to a heated vaporizer. The vaporized fuel then passed into the reformer which was essentially a heated stainless steel tube (5.5-in. long by 0.75-in. OD) containing 2-in<sup>3</sup> of the reforming catalyst. The reformed fuel was fed directly to the anode of a subscale fuel cell.

The reformer, when operated at 400°F and a space velocity of 500/h, was of sufficient size to provide fuel for five subscale cells.

For the initial tests, to measure methanol conversion as a function of temperature from 355°F to 400°F, the cell was disconnected and the reformer outlet was connected to a gas chromatograph. The results are given in Table 2. These data are in good agreement with a psuedo first order rate of reaction with respect to the methanol pressure:

$$\frac{w}{F_o k p_o} = \frac{1}{(1 + \epsilon)} \ln \frac{1}{1 - \alpha} + \epsilon \alpha$$

where:  $w$  = catalyst weight, g  
 $F_o$  = inlet flow rate of methanol, mole/sec  
 $p_o$  = inlet pressure of methanol, atm  
 $\alpha$  = fraction of methanol converted  
 $\epsilon$  = expansion factor (moles out-moles in/moles in)  
 $k$  = the rate constant (mole/g.cat., sec., atmosphere)

TABLE 2. METHANOL CONVERSION

OPERATING TEMPERATURE, °F	PERCENT CONVERTED
400	93.2
385	82.9
370	74.9
355	60.8

In previous work the rate constant was found to have an Arrhenius temperature dependence of the form:

$$k = 7.2 \times 10^7 \exp. (-27,030/RT)$$

Thus, the conversion,  $\alpha$ , can be related to the absolute temperature by the following expression:

$$1/T \propto \ln \left[ (1 + \epsilon) \ln \frac{1}{1 - \alpha} + \epsilon\alpha \right]$$

The close fit between this expression and the data in Table 2 is shown in Figure 8.

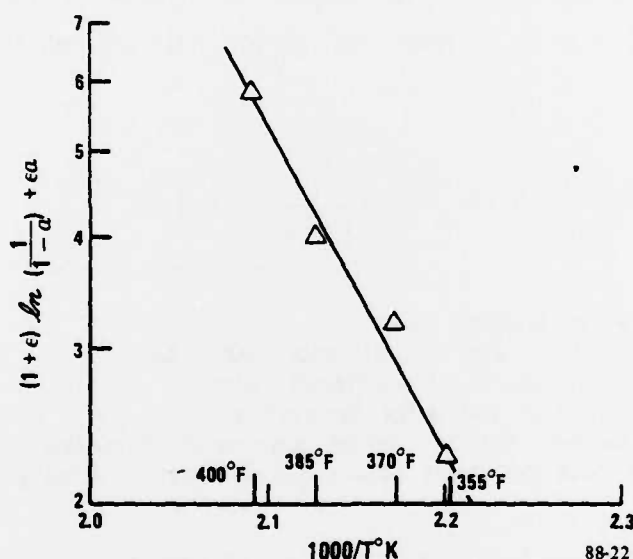


Figure 8. Methanol Conversion Dependence on Temperature

As a final test, the reformer was coupled to a subscale phosphoric acid fuel cell. Since the reformer output was sufficient to run five cells, eighty percent was discarded and only twenty percent was fed to the cell. The operating conditions are listed in Table 3.

TABLE 3. SUBSCALE CELL OPERATING CONDITIONS WITH REFORMED METHANOL FUEL

Oxidant/Utilization, %	-	Air/80
Fuel/Utilization, %	-	Reformed Methanol/70
Operating Temperature, °F	-	400
Operating Current Density, ASF	-	200
Reformer Temperature, °F	-	400
Fuel Feed	-	CH <sub>3</sub> OH/H <sub>2</sub> O = 1/1.3
Methanol Conversion Fraction	-	0.932

Both before and after running on the reformed methanol, the performance of the cell was checked out on a gas mixture (Table 1) which is commonly used at UTC to test fuel cells and catalysts. The test results are given in Table 4.

TABLE 4. CELL PERFORMANCE ON REFORMED FUELS

OPERATING CONDITIONS		CELL PERFORMANCE AT 200 ASF, mV
1.	Reformed Natural Gas/Air, Utilizations = 80/50	642
2.	MEOH-H <sub>2</sub> /Air, Utilization = 80/50 (Fuel Utilization Set Assuming 100% Conversion to H <sub>2</sub> )	624
3.	Same as 1, except Fuel Utilization = 85	640

The lower performance on reformed methanol relative to that on reformed natural gas is cathode-related as was to be expected from the Task 1 work. The loss was completely recovered within minutes, when the 70% H<sub>2</sub> fuel was substituted for the reformed methanol.

Since the methanol conversion falls off steeply with temperature, the reformer was operated at 400°F for all the cell tests. In one experiment the space velocity was reduced from 500/h to 300/h--corresponding to one reformer module feeding three rather than five cells. This had the effect of raising the conversion fraction to 96.5% and increasing the cell voltage by 10 mV.

It is concluded from the foregoing that a methanol/air fuel cell with thermally integrated internal reforming is viable.

#### FUTURE WORK AND RECOMMENDATIONS

From the standpoint of simplicity, the direct anodic oxidation is the most attractive way to use methanol as a fuel in a phosphoric acid fuel cell. The test results indicate that platinum-ruthenium is the best electrocatalyst for the direct anodic oxidation of methanol--at least on a weight basis. Further work on this bimetallic or alloy catalyst should be done to establish the optimum composition. Other alloys should also be examined.

The fact that the addition of steam to the methanol vapor greatly enhances the rate of oxidation implies that some form of steam reforming is involved even in direct oxidation. Difficulties arise because the catalyst is required to perform a double function--to promote not only the electrochemical oxidation, but also the methanol-water reaction.

An approach to internal reforming in the anode compartment might be by constructing a bilayer or hybrid electrode in which the layer of catalyst exposed to the raw fuel-steam mixture is totally hydrophobic and active for reforming, whereas the layer adjacent to the electrolyte has the hydrophilic/hydrophobic character

of a conventional gas diffusion electrode. The two layers might contain either the same or different catalysts. The development and testing of electrodes of this type is a possible topic for future work.

One requirement for the direct oxidation and internal reforming approaches is to prevent methanol from migrating across the cell to the cathode--unless one is prepared to accept some loss of fuel and to operate at high air flow rates to prevent severe cathode polarization. The obvious solution is to introduce a semi-permeable diaphragm such as an ion exchange membrane between the electrodes to stop, or at least hinder, the flow of methanol from the anode to cathode. Candidate barriers should be sought and evaluated in subscale cells.

The thermally integrated reforming concept shows considerable promise for both near- and long-term power plants. The next step is to design and build a small stack operating on this principle to uncover any problems which may have been overlooked in testing the simple configurations.

For all three systems--direct oxidation, internal reforming, and thermally integrated reforming--a method for returning some of the steam from the exhaust gases to the anode chamber or reforming module is needed, and power plant startup procedures also need to be considered.

## REFERENCES

1. N. A. Hampson, M. J. Willars, B. D. McNicol, The Methanol-Air Fuel Cell: A Selective Review of Methanol Oxidation Mechanisms at Platinum Electrodes in Acid Electrolytes, *J. Power Sources* 4 (1979) 191.
2. B. D. McNicol, *J. Electroanal. Chem.* 118 (1981) 71.
3. A. Weickowski and J. Sobkowski, Comparative Study of Adsorption and Oxidation of Formic Acid and Methanol on Platinized Electrodes in Acidic Solution, *J. Electroanal. Chem., Interfacial Electrochemistry* 63 (1975) 365.
- 4a. M. M. P. Janssen and J. Moolhuysen, Platinum-Tin Catalysts for Methanol Fuel Cells Prepared by a Novel Immersion Technique by Electrodeposition and by Alloying, *Electrochimica Acta* 21 (1976) 861.
- 4b. M. M. P. Janssen and J. Moolhuysen, Binary Systems of Platinum and a Second Metal as Oxidation Catalysts for Methanol Fuel Cells, *Electrochimica Acta* 21 (1976) 869.
5. M. Watanabe and S. Motoo, Electrocatalysis by Ad-Atoms, Part II. Enhancement of the Oxidation of Methanol on Platinum by Ruthenium Ad-Atoms, *Electroanal. Chem. and Interfacial Electrochemistry* 60 (1975) 267.
6. K. J. Cathro, The Use of Platinum-Rhenium Catalysts for the Oxidation of Aqueous Methanol, *Electrochemical Technol.* 5 (1967) 441.
7. A. Katayama, Electrooxidation of Methanol on a Platinum-Tin Oxide Catalyst, *J. Phys Chem.* 84 (1980) 376.
8. B. D. McNicol, A. G. Chapman, R. T. Short, Pt/Sn Bimetallic Catalysts for the Electrooxidation of Methanol: Poisoning by Silicate and Phosphate Anions, *J. Applied Electrochemistry* 6 (1975) 221.
9. FCR-2536, Investigation of In-Situ Oxidation of Methanol in Fuel Cells, Bi-monthly Technical Status Report No. 1, D. A. Landsman, September 9, 1981.
10. H. R. Kunz and G. A. Gruver, *J. Electrochem. Soc.*, 122, (1975) 1279.
11. The Japan Economic Journal, November 11, 1980.

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